

Strongly Correlated Impurity Band Superconductivity in Diamond: X-ray Spectroscopic evidence for upper Hubbard and mid-gap bands

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In a recent X-ray absorption study in boron doped diamond, Nakamura et al. have seen a well isolated narrow boron impurity band in non-superconducting samples and an additional narrow band at the chemical potential in a superconducting sample. We interpret the beautiful spectra as evidence for upper Hubbard band of a Mott insulating impurity band and an additional metallic ‘mid-gap band’ of a conducting ‘self-doped’ Mott insulator. This supports the basic framework of a recent theory of the present author of strongly correlated impurity band superconductivity (SCIBS) in a template of a wide-gap insulator, with no direct involvement of valence band states.

Recent discovery of superconductivity in boron doped diamond[1] by Ekimov et al., is a pleasant surprise and superconductivity is seen in a place where one suspected it the least. This discovery has important implications in basic science and technology. These results have been confirmed[2, 3] at an elevated superconducting T_c in doped thin films synthesized by microwave plasma assisted chemical vapor deposition (MPCVD), a method which has advantages over the original high pressure-high temperature synthesis. This paves way for a series of new experiments[3, 4, 5, 6] to unravel the mechanism of superconductivity in doped diamond as well as various anomalous properties that have been predicted theoretically[7]. One such first measurements is a recent X-ray absorption spectroscopy (XAS) in the non-superconducting and superconducting dopings, by Nakamura et al[5, 6].

Unique among theoretical proposals[7, 8, 9, 10, 11, 12] for the mechanism of superconductivity in this unusual system is a suggestion of the present author[7] that superconductivity here is an impurity band phenomenon driven by strong electron correlation effects. It has raised important questions on the origin and mechanism of superconductivity, by pointing out[7] that the disordered superconducting state is in the vicinity of the Mott insulator-metal transition point[13, 14].

In the XAS study in reference[5, 6], a well isolated narrow boron impurity band is seen in non-superconducting samples and an additional narrow band at the chemical potential is seen in a superconducting sample. In this letter we interpret the spectra and provide evidence for an upper Hubbard band of an impurity band Mott insulator and an additional metallic ‘mid-gap band’ of a conducting ‘self-doped’ Mott insulator. This interpretation that is simple and natural supports the basic framework of a recent theory of the present author[7] of superconductivity in a correlated impurity band in a template of a wide-gap insulator, with no direct involvement of valence band states, after the depletion of impurity states from the original broad valence band. We also discuss briefly at the end why an interpretation of the data in terms of certain lattice ‘relaxed’ hole states may not be tenable.

On doping, a boron atom substitutes a carbon atom and bonds to neighboring carbon atoms through sp^3 hybridization. As boron has one less electron compared to carbon, a hole (an unpaired spin) is left behind, in an otherwise filled band. In the ground state this hole is bound to the boron atom in one of the three fold degenerate impurity state with a binding energy of 0.37 eV. As more and more boron atoms are doped, the impurity wave functions overlap and there is an Anderson-Mott insulator to conductor transition at a critical boron concentration n_c , in this uncompensated semiconductor. The present author pointed out that since superconductivity observed in reference[1] is at a boron density, strikingly close to this critical density n_c [13, 14, 15], superconductivity is likely to be an impurity band phenomenon, dominated by strong correlation physics within the impurity band sub system. We will call this as the strongly correlated impurity band superconductivity (SCIBS). We modeled SCIBS in terms of an effective repulsive Hubbard model and argued how resonating valence bond correlations[16] among spin- $\frac{1}{2}$ moments of neutral B^0 acceptor states and ‘self-doping’, a spontaneous creation of a small and equal number of nominal B^+ and B^- will lead to a Mott insulator to superconductor transition across a critical boron density n_c . In real systems there could be also compensation from donors such as nitrogen, phosphorus and certain boron clusters.

In what follows we will interpret the recent XAS results as giving a strong evidence for the presence of a correlated impurity band, an upper Hubbard band and creation of a ‘mid-gap band’ by a process of self doping of the Mott insulator across the Mott insulator superconductor transition point.

In XAS, an electron from filled 1s state of either boron (B-K edge) or carbon (C-K edge) is removed and placed at an empty state above the chemical potential by soft X-rays. We wish to probe the boron acceptor states close to the chemical potential. As boron has a strong sp^3 hybridization with carbon atoms, the impurity hole wave functions have a large radius of about 5 to 8 Bohr radius. Thus it has a large carbon wave function content.

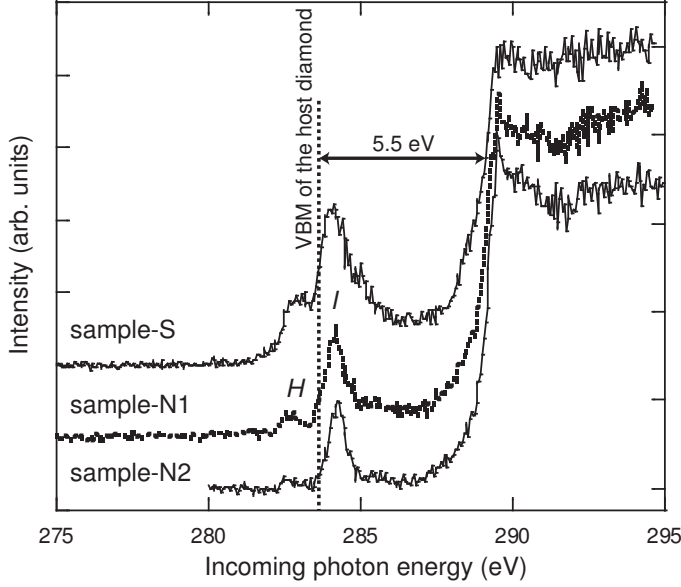


FIG. 1: The C-K XAS spectra of Nakamura et al.[5] is reproduced; S-superconducting sample and N1,N2 non-superconducting samples. The dotted line represents the energy of the valence band maximum using the band gap of 5.5 eV. Two characteristic peaks, *H* and *I*, are observed at about 282.6 and 284.1 eV. We interpret peak *I* as upper Hubbard band and *H* as the conducting mid-gap band of our impurity band subsystem (see text). Chemical potential lies within the small peak *H*, the metallic mid-gap band.

Further, in the range of concentration of interest acceptor wave functions start overlapping so that XAS on C-K edge are good enough to bring out the nature of states close to the chemical potential. It is clear from the experiments that C-K edge spectra has an advantage over B-K edge, as it has less contamination from deep levels from an unavoidable density of interstitial boron atoms and boron clusters.

Before we proceed, we would like to make two observations on the remarkable X-ray absorption spectra of reference[5]: i) for all three boron concentrations where experiments have been done, two non superconducting samples (below n_c) and one superconducting sample (above n_c), the impurity band retains its integrity and its center does not move. ii) at the chemical potential a new narrow band evolves and gets prominent in the superconducting state and the chemical potential is, surprisingly, pinned at an energy below the top of the valence band.

In what follows we discuss a simple theory of the shape of X-ray absorption and emission spectra of impurity band Mott insulator and conductor in the vicinity of the metal insulator transition point.

In XAS, the absorption cross section is determined, using Fermi golden rule and impulse approximation as

$$I_a(\omega) \sim \frac{2\pi}{\hbar} \sum_f |\langle i | \sum_{\ell} \frac{e}{c} \mathbf{p}_{\ell} \cdot \mathbf{A} | f \rangle|^2 \delta(E_f - E_i - \hbar\omega) \quad (1)$$

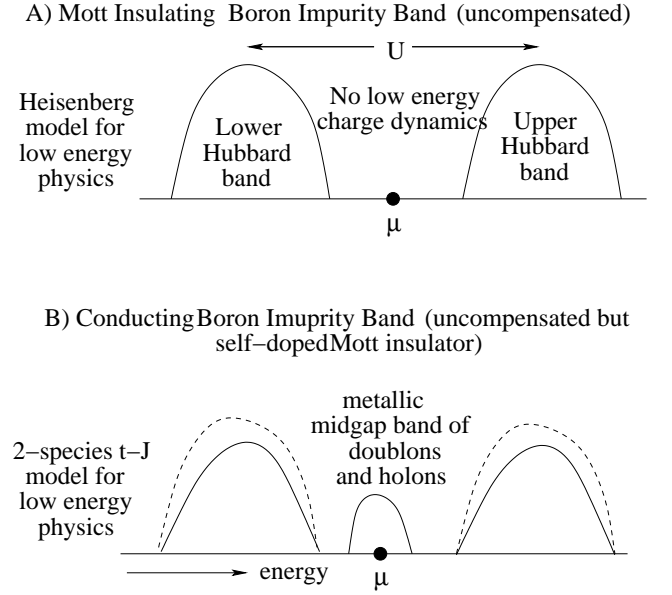


FIG. 2: Schematic local single particle spectral function of an electron in impurity band for two cases: A) Boron impurity band Mott insulator exhibiting upper and lower Hubbard bands and B) self-doped case, obtained by increasing boron density beyond Mott transition point; here mid-gap band contains equal number of holons and doublons, whose density depends on band parameters and long range coulomb interaction. Hubbard band splitting by U and chemical potential μ is also shown. In describing low energy physics, elimination of upper and lower Hubbards bands generates superexchange and we obtain a Heisenberg model for case A and a 2 species t-J model[18] for case B. A standard spectral sum rule keeps the total area under upper, lower and mid-gap bands the same in both cases.

We are interested in a narrow range of energy just above the chemical potential μ and ignore frequency dependence of matrix elements to get

$$I_a(\omega) \propto \rho_e(\omega), \quad \hbar\omega > \mu \quad (2)$$

where $\rho_e(\omega)$ is the local(atomic) one electron spectral function. The X-ray fluorescence or emission (XES) spectra, where electrons close to the chemical potential fall into the empty 1s-core hole state and emit X-rays, the emission intensity is given by

$$I_e(\omega) \propto \rho_h(\omega), \quad \hbar\omega < \mu \quad (3)$$

Here $\rho_e(\omega)$ is the local one hole spectral function.

Now we discuss the profile of the electron and hole spectral functions. At the energy scale of the impurity band width our discussion is rigorous and the spectral profile is qualitatively correct. These spectral features of a Mott insulator and doped Mott insulator are known from early Hubbard I to III approximations and recent infinite dimensional and dynamical mean field theory approaches[17].

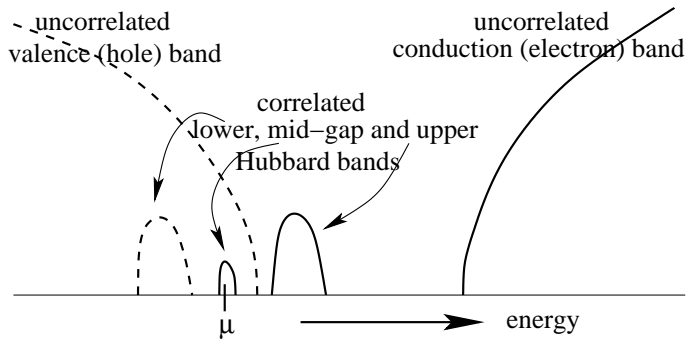


FIG. 3: We have overlaid the correlated Hubbard and mid-gap impurity bands with the one particle valence and conduction band density of states. Location of the chemical potential μ has meaning only within the Hubbard and mid-gap bands. As far the valence band it has no holes. XAS measures the conduction band, the upper Hubbard band and the mid-gap bands shown as thick lines.

In the atomic limit, $U \gg t_{ij}$, for a Hubbard model at half filling,

$$\rho_{e,h}(\omega) \sim \delta\left(\hbar\omega \pm \frac{U}{2}\right) \quad (4)$$

For our impurity Hubbard bands, disorder and finite t_{ij} will broaden the spectral function to give a shape shown in figure 2A. If we dope the ‘half filled’ impurity band with electron (doublons), for example by a small amount of compensation by an additional nitrogen doping, we introduce a band of mid-gap states, whose area is proportional to the compensation (dopant) fraction x . Mid gap states of a paramagnetic state are correlated many body energy levels and have no single particle description, for example in a Hartree-Fock theory. The low energy dynamics of the metallic band of mid-gap states (doublons) in this case of partial compensation by nitrogen is governed by t-J model. This is because, when we eliminate the surviving upper and lower Hubbard bands of a doped Mott insulator to obtain low energy effective Hamiltonian, superexchange gets generated.

In a recent paper we suggested[18], based on experimental results and theoretical considerations on Mott insulator to metal transition, that the conducting side close to the first order Mott transition point should be viewed as a ‘self doped’ Mott insulator. As the doping is internal, number of negative and positive (doublons and holons) carriers are the same. The carrier density is determined by long range coulomb interactions and band parameters. To describe the low energy dynamics of such a doped Mott insulator, which preserves superexchange in the conducting state, we introduced a 2 species t-J (or 2t-J) model. The schematic spectral profile, figure 2B, is the same as regular t-J model except that the mid-gap metallic band contains equal number of positive (holon) and negative (doublon) carriers (with refer-

ence to neutral Mott insulator). As mentioned earlier, in reality there can be a small amount of compensation from impurities such as nitrogen, phosphorus and certain boron clusters. The resonating valence bond physics of superconductivity in our self-doped Mott insulator[18] is partly contained in the t-J-U model[19], but with key differences.

X-ray absorption spectroscopy measures the upper Hubbard band and the conducting ‘mid-gap band’. X-ray emission spectroscopy measures the lower Hubbard band the conducting ‘mid-gap band’. However, in the case of acceptor impurity band, such as ours, emission from the close by valence band will mask the small signal from the impurity bands, making XES problematic. In the same vein, if we had a donor band XAS, rather than XES will have problems.

Now we discuss the experimental result of reference[5], figure 1, in the light of the above discussion. The spectra are for three boron dopings, two non-superconducting and one superconducting cases. The conduction band edge and the impurity bands are clearly visible. In the non-superconducting and superconducting samples the impurity band remains sharp, denoted by the peak I . This is our upper Hubbard band. In the superconducting state we have the additional band, at the chemical potential, which we identify as the metallic mid-gap band of self doped carriers, denoted by peak H . From the experimental result, we see that the peak to peak distance of the upper Hubbard band and mid-gap band, $\frac{U}{2} \approx 0.7$ to 1 eV. This value of $U \sim 1$ to 2 eV for our impurity orbital is easily rationalized, as the impurity Bohr radius of our deep level acceptor state is increased only by a factor of 5 to 8 from atomic Bohr radius.

Since $U \sim 1$ eV is large compared to acceptor binding energy $E_B \approx 0.37$ eV, an important question in the conducting state about possible hole transfer to top of the valence band arises. That is, soon after metallization increased charge fluctuations in the impurity band will introduce the Hubbard U repulsion energy among the holes by an amount $\sim xU$ prompting hole transfer to the valence band. Here x density of self doped carriers. In addition to this energy loss on metallization, there are two sources of energy gain; i) the well known delocalization energy, proportional to the impurity band width and ii) a Madelung energy gain[18] within the impurity band arising from long range coulomb interaction E_{Md} . This energy is missed in a Hubbard model, which ignores long range coulomb interaction; it is this which also determines the self doping fraction x . When $xU - E_{Md} > E_B$, it will be energetically favorable to drain holes from the impurity band to the top of the valence band.

In the experiments[5], the chemical potential neither falls on top of the valence band nor inside the impurity band, but seems to be pinned to the metallic mid-gap band. This means all low energy charge and spin actions are taking place within the impurity band. This is a

good support for our impurity band modeling[7] of the superconductivity phenomena. One may safely say that there are no hole fermi surface from a finite density of valence band holes, as is assumed in current electron-phonon theories[8, 9, 10, 11].

At this point it is also important to make a qualitative difference between a renormalized one particle band such as the conduction or valence band and a correlated many body bands such as upper, lower and mid-gap Hubbard bands. A finite value of spectral functions in these many body bands are basically projected one particle density of states rather than one particle level densities. We emphasize this in figure 3, where we overlay the correlated Hubbard and mid-gap impurity bands on the one particle valence and conduction band density of states. Location of the chemical potential μ has meaning only within the Hubbard and mid-gap bands. As far the valence band it has no holes. This figure also shows the mid-gap band, upper Hubbard band and the conduction band that will be seen in the X-ray absorption spectra by a thick line.

The authors of the XAS experiments[5] suggest that what we call as the mid-gap band at the chemical potential could arise from certain lattice relaxed hole states in the absence of simple rigid band shifts on doping. Unfortunately the energy of the hole is shifted in the opposite direction and it does not look like a relaxed state but a ‘strained metastable state’ which could decay down to the top of the valence band (energy of a hole is always positive and measured from the chemical potential). How, on metallization such a meta stable hole states will collectivized and become stable? That too in the background of an impurity band that continues to be present, as the XAS spectra indicates. One also has to answer why relative density of such lattice relaxed hole states (area under mid-gap band relative to impurity band) should increase with boron doping.

It is also not clear whether a phase separation of boron impurities will explain the observed XAS spectra. Indeed, some careful analysis has been done in the experiments[5] to eliminate the possibility of precipitation.

In all our discussion we did not discuss disorder explicitly. As emphasized in our original paper, the uncompensated case under discussion has a commensurate filling of the impurity band, with an average of one hole per boron atom. In such a situation Mott-Hubbard correlations overwhelm; disorder to a large extent is ‘irrelevant’ in the renormalization group sense. That is, once Mott localization sets in, Anderson localization has lesser role to play. Further, spin charge decoupling, an inevitable consequence in the Mott transition region, also protects current carrying holon and doublon states from Anderson localization effects. As we move far away from commensurate situation, for example by partial compensation, Anderson localization effects and notions such as mobility edge become important.

To summarize, it is indeed nice to have diamond, a relatively ‘simple’ system as a template for the fascinating impurity band Mott phenomena and superconductivity. A large band gap and a relatively large acceptor binding energy of a simple acceptor boron, nicely isolates out and makes the impurity Hubbard bands and mid-gap bands visible in X-ray absorption spectroscopy. It will be very nice to increase the energy resolution and explore some of the beautiful many body issues related to our mechanism[7] of SCIBS by X-ray absorption and emission spectroscopy, for a range of boron doping and also partial compensation.

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